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Polymers Used in Preparation of Nanofibers

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ABSTRACT

Polymer-based nanofibers as an important group of materials have attracted considerable attention of research and industrial areas. Polymer nanofibers with diameters in submicrometer (<1 μm) possess unique properties including large specific surface area per unit mass, which facilitated adding functionalities to surface for specific application.

Typically, polymer nanofibers have been synthesized by electrospinning, spinneret-based tunable engineered parameters (STEP) or drawing techniques, template synthesis, phase separation/inversion, self-assembly, solution blowing (air jet spinning), forcespinning (centrifugal spinning), and interfacial polymerization of nanofibers. The most common method is electrospinning due to its feasibility, cost-effectiveness, ability to fabricate continuous fibers from various polymers, and mass production. Polymer nanofibers are fabricated from both natural and synthetic polymers.

KEYWORDS: *Polymer, Nanofibers, Preparation, Fabrication*

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Introduction of Nanofibers

Nanofibers are fibers with diameters in the nanometer range (typically, between 1 nm and 1 μm). Nanofibers can be generated from different Polymers and hence have different physical properties and application potentials. Examples of natural polymers include collagen, cellulose, silk fibroin, keratin, gelatin and polysaccharides such as chitosan and alginate.[1][2] Examples of synthetic polymers include poly(lactic acid) (PLA), polycaprolactone (PCL),[3] polyurethane (PU), poly(lactic-co-glycolic acid) (PLGA), poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV), and poly(ethylene-co-vinylacetate) (PEVA).[1][2] Polymer chains are connected via covalent bonds.[4] The diameters of nanofibers depend on the type of polymer used and the method of production.[5] All polymer nanofibers are unique for their large surface area-to-volume ratio, high porosity, appreciable mechanical strength, and flexibility in functionalization compared to their microfiber counterparts.[1][2][6] There exist many different methods to make nanofibers, including drawing, electrospinning, self-assembly, template synthesis, and thermal-induced phase separation. Electrospinning is the most commonly used method to generate nanofibers because of the straightforward setup, the ability to mass-produce continuous nanofibers from various polymers, and the capability to generate ultrathin fibers with controllable diameters, compositions, and orientations.[6] This flexibility allows for controlling the shape and arrangement of the fibers so that different structures (i.e. hollow, flat and ribbon shaped) can be fabricated depending on intended application purposes. Using an innovative melt processing method, which is appropriate for the industrial mass production, scientists and engineers at the University of Minnesota, have been able to make nanofibers as thin as only 36 nm.[7]

Nanofibers have many possible technological and commercial applications. They are used in tissue engineering,[1][2][8] drug delivery,[9][10][11] seed coating material,[12][13][14] cancer diagnosis,[15][16][17] lithium-air battery,[18][19][20] optical sensors,[21][22][23] air filtration,[24][25][26] redox-flow batteries [27] and composite materials.[28]

Polymers used in Nanofibers Formation:

Natural Polymers:

1. Chitosan

Chitosan (CS) is a natural cationic polyelectrolyte copolymer that can be obtained by the deacetylation of its parent polymer chitin, a naturally occurring source derived from the exoskeleton of insects, crustaceans, and certain fungi. The abundance as a renewable resource and excellent properties, such as haemostasis, biodegradability, biocompatibility, non-toxicity, and chelation with metals, render chitosan suitable for biomedical applications. Moreover, chitosan has also shown good performances in inhibiting the growth of a wide variety of yeasts, fungi, and bacteria as well as gas and aroma barrier properties in dry condition. All these positive features of chitosan have provided ample opportunities for further development in biomedical and other industrial fields. [29-31]

It has been reported that pure chitosan fibers can be produced in nonaqueous solvents. For example, electrospinning of pure chitosan was successfully achieved in trifluoracetic acid (TFA) by Ohkawa et al. [32] Sencadas et al. improved the homogeneity of the nanofibers by adding dichloromethane to the chitosan/ TFA mixtures and systematically studied the processing parameters to set the ground for a reproducible way to obtain chitosan nanofibers for specific applications [33].

However, electrospinning individual chitosan from its aqueous solution remains a challenge. First, the rigid D-glucosamine repeat unit, high crystallinity, and ability to form strong hydrogen bond of chitosan make it difficult to be dissolved in most solvents. In addition, its polycationic properly also leads to high viscosity, which hinders the formation of sufficient chain entanglements and results in the formation of nanobeads rather than nanofibers [34]. However, the solvents for the spinning of the pure chitosan are environmentally harmful [35].The electrospinning for chitosan can only be achieved at concentrations in the range between 2% and 8% (wt/v). This urges us to develop new versatile methods for the electrospinning of chitosan at higher concentrations to ensure the mechanical stability and retain the bioactivity of its nanofiber products [36].

Therefore special attention needs to be paid to improving the spinnability of chitosan. Attempts have been made by blending chitosan with synthesized polymers, such as polyethylene oxide (PEO), polyvinyl alcohol (PVA), and PLA, and renewable polymers such as gelatin, alginate, and silk fibroin and nanoparticles to improve the mechanical strength, antibacterial activity, and antiadhesive properties towards bacteria of its nanofibers [37].

PVA is a typical nontoxic and water-soluble synthesized polymer with high biocompatibility and hydrophilicity. More importantly, PVA has good mechanical properties [38]. Liu et al. explored the preparation of PVA/chitosan hydrogel nanofibers by solution blowing method with ethylene glycol diglycidyl ether (EGDE) as cross-linker at various concentrations (as shown in Figure 8) and found that CS/PVA hydrogel nanofiber mats possessed the properties of both hydrogel and nanofiber mats. In addition to the similar excellent exudate absorption property to that of hydrogel films, hydrogel nanofiber mats allowed gaseous exchange, which decreased with the increase of its cross-linking degree (DCL). Moreover, CS/PVA hydrogel nanofiber mats demonstrated good antibacterial rates of over 81% against *E. coli*, which was not significantly affected by DCL. The findings suggest that the CS/PVA nanofiber hydrogel is a promising material for wound dressing [38].

Compared with synthetic polymers, natural polymers have better biocompatibility and lower immunogenicity. Sericin is one of the biodegradable and biocompatible natural polymers with good antioxidant, moisture absorption, and antibacterial and UV resistance properties and has been widely used in cosmetics and fabrics. Zhao et al. prepared chitosan/sericin composite nanofibers by blending binatural polymers and electrospinning to enhance their biological performance. The nanofibers had diameters ranging from 240 nm to 380 nm and continuous and uniform diameter distribution. Bioassays indicated that these novel composite nanofibers showed noncytotoxicity and remarkably enhanced cell proliferation and antibacterial activities against both Gram-negative bacteria *Escherichia coli* and Gram-positive bacteria *Bacillus subtilis* [39].

2. Cellulose

Cellulose is one of the most abundant biodegradable materials and can be extracted from different natural sources, such as wood and cotton pulps, via chemical or physical methods [40].

Bacterial cellulose (BC) is natural cellulose synthesized by acetobacter xylinum [40] and has high biocompatibility and transparency, nontoxicity, and excellent mechanical strength. Moreover, BC fibers have a very high surface area per unit mass, which, combining with its high hydrophilicity, leads to a very high liquid loading capacity. Thus, BC has been applied in various fields [41]. Costa et al. carried out electrospinning of acetylated BC nanofiber mats to produce artificial symmetric nanoporous structures. The SEM images revealed that nanopores were more uniformly distributed throughout the electrospun

nanofiber mat than those casted with BC mats. In addition, the electrospinning of modified BC nanofibers was easier than that of unmodified BC nanofibers, which could be explained by the dissolution mechanism of cellulose in DMA/LiCL solvent system [42]

However, BC shows poor antibacterial, antioxidant, and conducting and magnetic properties, which limits its application in biomedical and electronic fields [43]. One of the solution is to blend BC with other substances to promote its properties. Carbon nanotubules (CNTs) have been of great interest in various fields since their discovery. They are promising fillers for polymer matrices to prepare CNTs-reinforced composite materials because of their extraordinarily high aspect ratio, elastic modulus, and high axial strength. Chen et al. prepared multiwalled CNTs-embedded BC nanofibers (MWCNTs/BC nanofibers) by electrospinning. The TGA analysis showed that the initial temperature of degradation followed the increasing order of BC < electrospun BC nanofibers < electrospun MWCNTs/BC nanofibers, which was attributed to the crystalline polymorph transformation and orientation as well as the embedded MWCNTs. In addition, the mechanical properties including tensile strength and Young's modulus and electrical conductivity of the products were significantly enhanced due to the well-dispersed and aligned MWCNTs. The finding indicates that MWCNTs/BC nanofibers may be potentially used in medical, mechanical, and electrical fields.[44]

Cellulose Acetate (CA) is a derivative of cellulose and has good stability and solubility in organic solvent. It can also selectively absorb low-level organic compounds and toxins. However, CA has poor mechanical properties [45].

3. Alginate

Alginate is a natural linear polysaccharide copolymer and can be obtained from brown sea weed. Sodium alginate (SA) has been well studied on its biomedical application due to its superior properties including biocompatibility, biodegradability, nontoxicity, hydrophilicity, and low cost. Unlike chitosan, alginate is highly soluble in water [46].

To improve the structural integrity of the prepared nanofibers, alginate-based materials are usually cross-linked with divalent ions, such as calcium and barium. In addition, double cross-linking with glutaraldehyde, hexamethylene diisocyanate (HMDI), epichlorohydrin, and adipic acid (ADA) hydrazide has also been proposed. Unlike the non-cross-linked electrospun nanofibers are highly soluble and relatively insoluble in both water and simulated body fluid [47-49].

However, pure SA nanofibers have been rarely fabricated via electrospinning. Nie et al. [50] prepared smooth and uniform alginate nanofibers by introducing glycerol as cosolvent and simply adjusting the volume ratio between glycerol and water. Fang et al. [51] reported that pure alginate had been successfully electrospun by introducing Ca^{2+} cations to SA aqueous solutions. They demonstrated that high intermolecular interactions and low surface tension were the critical factors to improve the electrospinnability of SA solutions.

Alginate has poor properties including low mechanical strength, high degradation rates, and processing difficulties, which are usually overcome by compositing alginate with other polymers such as PEO [52] and PVA. It can be attributed to the intermolecular hydrogen bonds formed between the polymers and alginate. Surfactants, such as lecithin [53], and cosolvents have also been proposed to facilitate its processing for the preparation of nanofibers [54].

4. Gelatin

Gelatin (GT) is a renewable polymer obtained by the partial hydrolysis of collagen, a most abundant natural substance in connective tissues. GT has been widely used as a bioengineering material due to its high biocompatibility, biodegradability, and low cost. GT can also prevent fluid loss, which plays an important role in wound healing [55-57]. However, the electrospun gelatin nanofibers are soluble in water and have poor mechanical strength [57,58]. Therefore, cross linking treatments have been adopted to increase their water resistance and mechanical properties [59,60]. The cross linking can be realized by physical processes, such as drying, heating, γ-ray, electron beam, and UV light exposure and chemical treatments by using cross-linker, such as formaldehyde, glutaraldehyde (GA), epoxy compounds, tannic acid, carbodiimide, acyl azide, and transglutaminase [61], through dissolving gelatin in 2,2,2-trifluoroethanol [62], formic acid dope solution [63], and water-based cosolvent composed of ethyl acetate and acetic acid [64]. Among all chemicals, GA is by far the most widely used due to its high efficiency, easy accessibility, and low cost. However, glutaraldehyde at high concentrations is cytotoxic and can disrupt the electrospun fiber morphology [65]. Ko et al. [61] demonstrated that the gelatin nanofibers cross linked with 0.5% (w/v) genipin promoted cell proliferation and reduced its solubility and cytotoxicity. Lu et al. [66] fabricated gelatin nanofibers by electrospinning and compared the properties of the gelatin nanofibers cross-linked by vapour and liquid-phase GA. Their results indicated

that the cross-linking by both vapour-phase and liquid-phase GA was able to improve the mechanical strength of the gelatin fibers. The cross linking with liquid phase GA resulted in more evenly cross-linked, close packed, and higher tensile. The excessive cross-linking with vapour-phase GA led to membranes shrinking due to poorly cross-linked middle layers in their hierarchy structure. Therefore, a novel *in situ* cross-linking method was proposed by Slemming-Adamsen et al. [67] for the fabrication of electrospun gelatin nanofibers with 1-ethyl-3-(3-dimethylaminopropyl)-1-carbodiimide hydrochloride (EDC) and N-hydroxysuccinimide (NHS) as cross-linkers. Kwak et al. [68] prepared *Phaeodactylum tricornutum* (*P. tricornutum*) extract-loaded gelatin nanofibers via electrospinning. *P. tricornutum* is a diatom which exists in brackish and marine water worldwide. The water-soluble extracts of *P. tricornutum* have showed anti-inflammatory, analgesic, and free radical scavenging activities. The introduction of *P. tricornutum* extracts improved the conductivity of the gelatin solution and reduced the diameter of the nanofibers. Their results also confirmed the antimicrobial activity and noncytotoxicity of the *P. tricornutum*-loaded gelatin nanofibers.

Gelatin has also been used as a blend component to prepare nanofibrous membranes for tissue scaffolds, wound healing and health caring devices, and other biomedical applications. Shan et al. [69] prepared silk fibroin/gelatin (SF/GT) electrospun nanofibrous dressing loaded with astragaloside IV (AS), an effective component, to accelerate wound healing. They found that the nanofibers were able to significantly improve cell adhesion and proliferation, promote wound healing, induce proangiogenesis of partial thickness burn wound, and inhibit complications in wounds. In addition, SF significantly decreased the average diameter, degradation rate, and the facture strain under high break strength of the produced nanofibers.

In addition, to the general properties of a condensed polyphenol, the grape seed polyphenol (GSP) has some unique properties, such as antimicrobial activity, anti-inflammatory activity, and reducing blood sugar and fat. Han et al. [70] fabricated GSP/gelatin composite nanofibers containing Ag-NPs by electrospinning as a novel biomaterial. GSP served as the reducing agent and stabilizing agent for silver nanoparticles. The electrospun composite nanofibers had average diameters in the range of 150-230nm and a uniform distribution of Ag-NPs with an average diameter of 11nm that contributed to their good antibacterial performance. Further investigation also revealed that the composite nanofibers containing silver nanoparticles had no toxicity at such concentrations. Thus, they could be potentially utilized in biomedical field as a wound dressing.

5. Hyaluronic Acid

Hyaluronic acid (HA) is one main glycosaminoglycan which is found in the ECM of many soft tissues of higher animals [71]. HA can decrease the formation of postsurgical adhesions due to its noncoagulant activity, modulation of fibrous tissue, barrier effect on fibrinogen, and inhibitory effect on the superoxide release from granulocytes [72]. Previous studies have demonstrated that HA nanofiber wound dressing showed better performance than the solid HA in wound healing due to its unique morphologies. However, HA solutions have high solution viscosity even at low concentrations, leading to issues in the production of consistent nanofibers [73].

Brenner et al. prepared pure HA nanofibers by electrospinning in a solvent system of aqueous ammonium hydroxide (25% NH_4OH) and DMF at pH of 11 to eliminate the solvent induced degradation effects on the biopolymer as reported in the previous studies. Continuous, cylindrical, and randomly oriented pure HA nanofibers with a diameter of 39 ±12nm and good biocompatibility were successfully electrospun [71].

Uppal et al. fabricated HA nanofibers by electrospinning with deionized water as a solvent and cocamidopropyl betaine as a surfactant. Based on the report of histopathologist, the sterilized HA nanofibers wound dressing showed better pathology performance than other sterilized wound dressings including solid HA, gauze with Vaseline dressing, adhesive bandage, and antibiotic wound dressing. The evaluation criteria included epithelial tissue gap, epithelial tissue detachment from the dermis, the presence of granulation tissue, and the assessment from clinic photographs based on the color of the wound and whether the wound was fully covered or not by the epithelial tissue. In addition, it showed higher air permeability than sterilized solid HA and gauze with Vaseline dressing, which contributed to the faster wound healing [73]. In all, the addition of antibiotic components could lead to better performance of HA nanofibers.

Chen et al. prepared dual functional core-sheath structured nanofibers with HA as the inner core and Ag-NPs-loaded PCL as external sheath by coaxial electrospinning. This design was used to control the slow release of HA from the core to mimic the biological function of HA in synovial fluid containing high concentration of HA. The sheath acted as a barrier with antimicrobial activity to prevent infection

and alleviate adhesion. The results demonstrated that the core-sheath structure met the need of preventing peritendinous adhesion and postoperative infection through the slowly released HA and rapid release of Ag-NPs without exhibiting significant cytotoxicity [72].

6. Collagen

Collagen is the principal structural element of the native ECM in a three-dimensional network structure composed of multifibrils in a nanofiber scale. Due to a wealth of merits including biological origin, nonimmunogenicity, and excellent biocompatibility and biodegradability, collagen has been widely used as biomaterials in pharmaceutical and medical fields such as carriers for drug delivery, dressings for wound healing, and tissue engineering scaffold. Among all isoforms of collagen, the fibrillar structure of type I collagen has long been known for its important roles in cell attachment, proliferation, and differentiation.[74,75].

The adaptations of electrospinning to produce tissue engineering scaffolds composed of collagen nanofibers have shown that the structural properties of the electrospun collagen vary with the tissue of origin, the isoform, and the concentration of the collagen solution [76].

Collagen-composite fibrous mats have been fabricated with PEO [77], PCL [78,79], polylactide-polyglycolide (PLGA) [76], poly(L-lactide-*co*-ε-caprolactone) (PLCL) [80] chitosan [74], hydroxyapatite [81, 82], and poly(L-lactic acid)-co-poly(ε-caprolactone) (P(LLA-CL)) [83]. Chen et al. [84] prepared the composite nanofibrous membrane (NFM) of type I collagen, chitosan, and PEO by electrospinning, which was further cross-linked with GA vapor. The cross-linking increased Young's modulus of the NFMs and decreased their ultimate tensile strength, tensile strain, and water sorption capability. The NFMs showed no cytotoxicity toward the growth of 3T3 fibroblasts and demonstrated good biocompatibility *in vitro*. In addition, the NFMs showed wound dressing for skin regeneration. Choi et al. [79] examined the feasibility of using PCL/collagen based nanofibers as a scaffold system for implantable engineered muscle organization. Their results showed that, in contrast to the randomly oriented nanofibers, unidirectionally oriented nanofibers could induce muscle cell alignment and myotube formation. The aligned composite nanofiber scaffolds seeded with skeletal muscle cells may be able to provide implantable functional muscle tissues. Liu et al. [85] explored the incorporation of neurotrophin (NT-3) and chondroitinase ABC (ChABC) into the electrospun collagen nanofiber for spinal cord injuries (SCI) treatment. The sustained release of NT-3 and ChABC for at least 28 days was achieved. Such biofunctional scaffolds may be found useful in SCI treatment by providing topographical and multiple biochemical cues to manipulate the growth inhibitory environment and promote axonal regeneration.

7. Silk fibroin

Silk fibroin (SF) is a main component of silk. It is a type of fibrous protein with remarkable mechanical properties produced in the form of fiber by silkworms and spiders. SF is also a promising wound dressing material due to its excellent mechanical properties, as well as its biocompatibility, controllable biodegradability, water-based processing, morphologic flexibility, and easily accessible chemical groups for functional modification. Despite its advantages, the low availability of SF limits the industrial scale production of its biomaterials. Generally, the electrospun SF fibers with desirable properties for bioengineering are prepared with SF at very high concentrations in the range of 20-40%. In addition, the highly crystalline *β*-sheet secondary structures result in the insolubility of SF, which limits its biomedical applications. Therefore, electrospun SF nanofibers are usually chemically treated with methanol[86], ethanol, propanol [87], and water vapour [88] to increase their stability. Strategies have been proposed to increase the viscoelasticity of SF systems by blending them with other polymers, which improves the mechanical properties while maintaining the biocompatibility of the obtained nanofibers [89-92].

Calamak et al. [93] fabricated silk fibroin nanofibers containing UV-reduced Ag-NPs by electrospinning method and post treated the product with methanol and GA vapour. The post treatments promoted the mechanical properties of the SF bionanotexiles. The results indicate that the methanol treatment was more effective in the crystallization transition of fibroin from random coil to *β*-sheet. In addition, Ag-NPs significantly decreased the diameter of the nanofibers and contributed to their antibacterial activity against Gram-positive bacteria *S. aureus* and Gram-negative bacteria *P. aeruginosa*.

Polyethylenimine (PEI) is a polycationic antimicrobial polymer with interesting ability to enter cells or permeabilize cell membranes. Calamak et al. [91] prepared silk fibroin based antibacterial bionanotextiles and explored their application as wound dressing materials. The addition of PEI to the nanofibers decreased the average diameter of the nanofibers and increased their hydrophobicity, cell

viability, and antimicrobial activity against both gram positive and gram negative bacteria.

Shahverdi et al. [90] fabricated silk fibroin blended with PLGA nanofibers via a dual source electrospinning setup, through which the electrospinning of SF and PLGA nanofibers could be separately optimized and achieved. They found that the concentrations of SF and PLGA predominantly affected the formation of the bead structure in the fibers. The addition of PLGA significantly improved the mechanical properties of the nanofibers. The incorporation of SF with PLGA displayed better cell attachment, proliferation, and viability performance than pure SF nanofibers and pure PLGA nanofibers.

Synthetic Polymers :

1. Polyvinyl Alcohol (PVA)

Poly (vinyl alcohol) (PVA) is a non-carcinogenic synthetic polymer produced from vinyl acetate by hydrolysis, alcoholysis, or aminolysis It is used in a diversity of biomedical applications due to its biocompatibility, biodegradability, non-toxicity, hydrophilicity, and low tendency for protein adhesion [94]. It has been broadly utilized for tissue regeneration and drug delivery applications. Besides its excellent hydrophilic nature and fluid absorption ability, it also demonstrates an outstanding capability to be manipulated in the form of fibers, particles, sponges, textiles, and films. It has been employed in the formulation of polymer-based wound dressings to treat chronic wounds and acute injuries. Due to its attractive properties, PVA has been frequently utilized in biopolymer-based dressings to improve the mechanical performance of the dressing for wound healing and skin regeneration. Due to the strong affinity of PVA wound dressings for binding with glucose, some researchers suggested that it could be utilized to develop wound dressings to treat diabetic wounds. However, plain PVA–based wound dressings have an incomplete hydrophilic feature with insufficient elasticity and rigid structure, which limit its application alone as wound dressing scaffolds. Furthermore, some PVA–based wound dressings suffer from poor stability in water. Among the numerous wound dressing materials reported, wound dressings formulated from PVA combined with some biopolymers and some other synthetic polymers display attractive features, such as excellent biocompatibility, biodegradability, sustained drug release profiles, etc. [95].

Preparation of PVA Nanofibers : The basis material is PVA, which has a molecular weight of 72,000 g/mol. The PVA was used in the form of a PVA solution with concentrations of 8%, 10%, and 12%. Eight percent PVA solution was made by adding 8 grams of PVA into 100 ml of distilled water. Eight grams of PVA were mixed with 100 ml of distilled water to get an eight percent PVA solution. Ten grams of PVA were mixed with 100 ml of distilled water to make a 10% PVA solution. Twelve grams of PVA were mixed with 100 ml of distilled water to get a 12 percent PVA solution. The mixture was then agitated at 100°C until it was totally homogenous. Because PVA is hydrophilic, it may dissolve in water, adding aquadest to a PVA solution tries to dissolve it. The resultant solution was then electrospinning at 17 kV and 20 kV, with a distance of 7 cm, 10 cm, and 15 cm between the needle tip of syringe and the collector drum, and a flow rate of 5 ml/hour and the electrospinning process time is 1 hour.

2. Polycaprolactone (PCL)

Polycaprolactone (PCL) is a synthetic polymer that belongs to the class of aliphatic polyesterstogether with polylactide (PLA), polyglycolic acid (PGA), and poly (lactic-co-glycolic acid) (PLGA) [96]. PCL is a biocompatible and biodegradable polymer that has been investigated for wound healing and tissue regeneration applications. It stimulates quicker wound healing and decreases inflammatory infiltration [96]. Nonetheless, PCL biodegrades at a significantly slower rate in comparison with PLGA, PGA, and PLA. This slow biodegradation causes PCL to be less attractive for this type of biomedical application but more attractive for controlled-release, sutures, and long-term implant applications. Therefore, the combination of biopolymers with PVA or PCL to prepare hybrid nanofibers via electrospinning technique can result in interesting excellent properties that would be very suitable for wound healing and skin regeneration applications. The main limitation of PCL is poor cell adhesion and growth resulting from its hydrophobic surface. Therefore, it essential to blend PCL with natural polymers to enhance its cellular attachment and proliferation. The other disadvantage of PCL is weak antimicrobial effects that can be overcome by loading antibacterial agents such as antibiotics and metallic nanoparticles [97]. Polycaprolactone (PCL), a biodegradable and bio-compatible polymer with rheological and viscoelastic propertiessuperior to many bioresorbable polymer counterparts, has beenfabricated into a fibrous structure with the electrospinningmethod and applied for drug delivery, wound dressing, and tis-sue regeneration.However, in order to obtain bead-freenanoscale fibers, some highly toxic solvents such as chloroform,dimethylformamide, tetrahydrofuran, dichloromethane, andmixtures thereof have often been used in the electrospinning of PCL. The toxic effects of these volatile organic solvents bring aboutdangers to the operator, environment, and end

users.Severalattempts have been made to find alternative solvents to reducethe risk. Electrospinning of PCL dissolved in acetone,aceticacid/acetone,and formic/acetic acidyielded promisingresults of nanoscale fibers. Yet, when PCL is dissolved in glacialacetic acid (GAC), a much more benign solvent,only beadednanofibers or microscale fibers could be obtained unless a vol-atile toxic additive (pyridine) is used.On the other hand,some nonsolvents for PCL like methanol,ethanol,ordimethyl sulfoxide (DMSO)being mixed with good solventsto improve the processability of electrospinning have also beenreported. However, H2O with no toxic properties as a nonsol-vent for PCL has seldom been reported as an assistant to elec-trospinning of PCL. Nevertheless, previous reports showed thata PCL/chitosan homogeneous solution could be achieved byblending the PCL solution dissolved in GAC with a chitosansolution dissolved in 0.5 Macetic acid when the acetic acid con-centration is over. Thus it was supposed that PCL anda high concentration of acetic acid could form a homogeneoussolution. Compared to the PCL/GAC solution, the conductivityshould be increased after H2O is added for the ionization of theacetic acid, which is beneficial for electrospinning of nanofibers.

3. Polylactic Acid (PLA)

Poly (lactic acid) (PLA), poly (vinyl alcohol) and polycaprolactone are examples of biocompatible polymers. Due to its biodegradability, biocompatibility and spinnability, PLA is a widely used polymer in electrospinning processes in versatile biomedical areas[98-99] PLA can be easily dissolved in different kinds of conventional solvents such as acetone (AC), chloroform (CHL), dichloromethane (DCM), dimethylacetamide (DMAc), dimethylformamide (DMF), 1;4-dioxane (DX), tetrahydrofuran (THF). PLA can be produced by condensation polymerization and ring opening polymerization techniques. PLA obtained by condensation polymerization has low molecular weight and poor mechanical properties. Physical properties of PLA have shown excellent improvement with ring opening polymerization .Poly- L-lactic acid (PLLA) occurs with polymerization of L-lactide. Poly (lactide-co-glycolide) (PLGA) is one of the most commonly used copolymers of PLA in biomedical applications. PLGA occurs by copolymerization of PLA and polyglycolic acid (PGA). Nanofibers of PLA and PLA blends can be used in a wide variety of biomedical and biotechnological applications. Biomedical applications include drug release, scaffold for tissue engineering, dressings for wound healing and dental applications while biotechnological applications contain biosensors, molecular filtrations and preservations of biological agents.

4. Polyurethane (PU)

PUs contains urethane group (–NH–(C=O)–O–) in common while most PUs are thermosetting polymers, in contrast to thermosetting polymers, thermoplastic polyurethanes (TPUs) melt when they are heated and are easy to use in manufacturing processes. Varying the structure of PUs, their properties can be varied in a wide range [100]. PUs are formed by reaction of polyisocyanates with hydroxyl-containing compounds. Desired properties can be tailored by selecting the type of isocyanate and polyols, or combination of isocyanates and combination of polyols [100]. Strong intermolecular bonds make polyurethanes useful for diverse applications in adhesives and coatings, also in elastomers, foams, and medical applications because of their good biocompatibility. The factors determining properties of a polyurethane elastomer are: structure of the polyol, type of diisocyanate, type of the chain extender, molar ratio NCO/OH, soft-segment concentration, molecular weight of the polyol and filler. In polyurethane elastomers, chains are linear, and cross-linking was achieved by physical bonds and hard domain formation. They flow when they are melted and harden by cooling (thermoplastic behavior). Displaying reversible cross-linking, domains are destroyed above the melting point of the hard phase, but are reformed when they get cooled. These materials are called “thermoplastic urethanes” (TPUs) [100]. In addition to the linear TPUs, obtained from difunctional monomers, branched or cross-linked thermoset polymers are made with higher functional monomers. Linear polymers have good impact strength, good physical properties, and excellent processibility, but limited thermal stability. On the other hand, thermoset polymers have higher thermal stability, but sometimes lower impact strength [101]. The vast selection of polyols, isocyanates, and chain extenders allows PUs to be varied from soft thermoplastic elastomers to adhesives, coatings, flexible foams, and rigid thermosets. TPU elastomers are segmented block copolymers, comprising of hard- and soft-segment blocks. The soft-segment blocks are formed from long-chain polyester or polyether polyols and 4,4′,-methylenebis(phenyl isocyanate) (MDI); the hard segments are formed from short-chain diols, mainly 1,4-butanediol and MDI [101]. The unique properties of linear TPUs are attributed to their long-chain structure. TPUs are resilient elastomers of significant industrial importance, which possess a range of desirable properties such as elastomeric, resistant to abrasion, and excellent hydrolytic stability. PU is

often chosen as a material for composing a nanoweb due to its chemical stability, mass transport, good mechanical properties, and also excellent nanofiber forming characteristic. Electrospun PU nanofiber mats exhibiting good mechanical properties may have a wide variety of potential applications in high-performance air filters, protective textiles, wound dressing materials, sensors, in biomedical applications, drug delivery, etc.. It is also frequently used in wound dressing studies because of its good barrier properties and oxygen permeability. It has reported that semipermeable dressings, many of which are PU, enhance wound healing. Degradable and biocompatible aliphatic PU could also be formed into scaffolds via melt electrospinning. Beside these biomedical applications, the PU nanofiber filters were prepared by electrospinning process based on 3D particle filtration modeling and some theoretical predictions were obtained for the filtration efficiency [102]. In another study, PU cationomers (PUCs) containing different amounts of quaternary ammonium groups were synthesized and electrospun into non-woven nanofiber mats for use in antimicrobial nanofilter applications [103]. Varying the structure of PUs, the properties of PUs can vary in a wide range. The flexibility to tailor the structure during processing is one of the main advantages of PUs over other types of polymers. A lot of different types of PU used in electrospinning process, some of them were synthesized before electrospinning according to the researchers intended use and some of them were used as they received.

5. Poly-lactic-co-glycolic acid (PLGA)

PLGA is produced by the catalyzed ring-opening copolymerization of the LA and GA units. During polymerization the monomeric units are consecutively linked together through ester linkages, resulting in the formation of the PLGA copolymer [3,. PLGA is widely used in nanomedicine due to its biocompatibility and effective biodegradability, which occurs through the hydrolysis of the ester bonds of lactate and glycolate. These monomers can then be metabolized via the Krebs cycle, yielding nontoxic byproducts (H2O and CO2) [104,105]. Different forms of PLGA can be obtained by varying the Poly(lactic acid):Poly(glycolic acid) (PLA:PGA) ratio during polymerization; for example, PLGA 50:50, which is frequently used in nanotechnology, has a composition of 50% lactate and 50% glycolate. PLGA copolymers inherit the intrinsic properties of their constituent monomers, where the PLA:PGA ratio, along with the polymer molecular weight, influence their hydrophobicity, crystallinity, mechanical properties, size and biodegradation rate. PGA is a crystalline hydrophilic polymer, while PLA is a stiff and more hydrophobic polymer; therefore, PLGA copolymers with a higher PLA content are less hydrophilic, tend to absorb less water and consequently present longer degradation times [106]. The degradation time can vary from several months to several years depending on the molecular weight (Mw) and copolymer ratio. PLGA is soluble in a variety of solvents, including organic solvents such as chloroform, acetone, ethyl acetate and tetrahydrofuran. All the above-mentioned features of PLGA have been proven to be useful for several applications; controlled drug release in particular. PLGA can be block-polymerized with other copolymers, which can alter its behavior and physicochemical propert. Diblock or triblock copolymers have been developed to meet the need for better carrier functionality, both in terms of the variety of drugs incorporated and administration methods. Block copolymers of PEG (poly(ethylene glycol)) and PLGA are the most reported both in diblock (PLGA-PEG) [and triblock conformations (PLGA-PEG-PLGA or PEG-PLGA-PEG). The creation of PEG layers can reduce interactions with foreign molecules, increasing shelf stability in this way. However, it can also decrease drug encapsulation efficiencies. When compared with PLGA alone diblock copolymers have shown improved release kinetics. The random combination of other polymers with PLGA can also be beneficial; for example, combining biodegradable photoluminescent polyester (BPLP) with PLGA will make the system suitable for photoluminescence imaging [107]. Thus, it is important to consider the final purpose of a system when choosing a polymer conformation. Regarding the physical characteristics of nano-PLGA structures, they can be controlled by parameters specific to the production method employed. For example, the size of PLGA NPs can be determined to a certain extent by the concentration of polymer used for their synthesis. Surface functionalization is another important aspect that allows a certain control over particles' biocompatibility, biodegradation, blood half-life and, when applicable, targeting efficiency. In fact, PEGylation has been shown to improve the pharmacokinetic properties of drugs encapsulated into PLGA composites [108]; coating PLGA NPs with biocompatible hydrophilic polymers (PEG or chitosan) can enhance stability and circulation time while diminishing toxicity. In terms of biomedical applications, PLGA has been used in the clinic since 1989, being introduced mostly as microsphere formulations; however, PLGA implants and nanocomposites are also a reality. PLGA is mostly utilized for drug delivery, having ~20 formulations

that are FDA- and EMA-approved [109]. These are mainly administered by subcutaneous/intramuscular injections.

6. Polyvinylpyrrolidone

Polyvinylpyrrolidone (PVP) is widely employed as a multifunctional material and it was approved by the US Food and Drug Administration as a safe polymer for biological experiments due to its simple processability, biocompatibility, and non-antigenicity [110-111]. PVP was largely employed as a reinforcing material for biocomposites in a variety of applications, including bone tissue engineering, soft implants, biosensors, and artificial cartilage substitutes. PVP can also be used in the fabrication of PVA hydrogels-based composite scaffolds for bone tissue engineering. PVP has several advantages in the pharmaceutical fields, and it acted as a stabilizer, a protective agent, a binder, a lubricating, a crystallization inhibitor, and a bioavailability enhancer for several active pharmaceutical ingredients (API). It is widely known that PVP exhibited a higher solubility in water and polar solvents, and it also has a higher glass transition temperature (165 ± 1°C) and was chemically stable in dry conditions [112]. Such physicochemical properties of PVP make it a versatile polymer with effective abilities in pharmaceutical field. PVP was largely used to develop various drug delivery systems, including oral, topical, transdermal, and ophthalmic administration. PVP-based fibers composed of several active substances were successfully achieved [113]. PVP hydrogels, oral tablets, PVP films, composite nanoparticles, microcapsules, and microspheres [114] were also developed

Conclusion:

The nanofibers prepared from the renewable polymers and synthetic polymers can combine the excellent properties of the renewable polymers and nanofibers. They have become one of the most important materials used in wound dressing and attracted more and more attentions in recent years. The preparation methods, including electrospinning, bubbfil spinning, centrifugal spinning, and freeze-drying, have been widely used to prepare the nanofibers from the renewable polymers. Particularly the wound dressings prepared from chitosan, cellulose, alginate, gelatin, hyaluronic acid, collagen, and silk fibroin or their composites have been widely used as the wound dressing to promote wound healing, hemostasis, skin regeneration, diabetic ulcers, tissue engineering, and so on. Many of the dressings have been used in clinic. But for many renewable polymers which originated from natural components, there are many factors which influence the structure and property of the polymers and they are hard to be controlled. Although their properties are versatile, many of the properties are less prominent. When the renewable polymers are prepared to nanofibers and used for wound dressing, many of their properties, including antibacterial properties, hemostatic properties, biodegradability, cell adhesion and proliferation, and mechanical properties, need to be regulated by controlling the structure and properties of the nanofibers or compositing with other synthetic polymers to fit for the requirement of different wound. The above problems have become the future research keynotes for the nanofibers prepared from the renewable polymers.

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CONFLICT OF INTEREST:

All authors declared no conflict of interest for the work.

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